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Theory of concentration depolarization in the presence of orientational correlations

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A theory is presented that incorporates the effect of orientational correlations between luminescent molecules on the fluorescence depolarization due to incoherent energy transfer. The luminescent molecules are embedded in a homogeneous two- or three-dimensional medium which is in an axially symmetric phase with the xy plane as a symmetry plane, and consists of axially symmetric molecules. For the general orientational singlet distribution and the general form of orientational correlations consistent with these symmetries, we derive analytical expressions for the anisotropy of fluorescence emission. In a no back transfer model, numerical results are evaluated for a simple choice of correlations that tend to align nearby molecules. In a pure donor system, the anisotropy of fluorescence is found to be strongly dependent on these correlations. By ignoring them, the critical transfer distance, as obtained from depolarization experiments, may be drastically underestimated. In a system where donors are surrounded by a huge majority of traps, the critical transfer distance can be determined from the intensity of trap fluorescence. Its anisotropy also strongly depends on correlations and may thus give an indication of the correlation length scale.

I. INTRODUCTION

Fluorescence depolarization due to incoherent energy transfer between luminescent molecules embedded in a host medium (concentration depolarization) has been the subject of many experimental[1–4] and theoretical[5–11] investigations. To our knowledge, all theoretical studies so far are limited to systems in which both positions and orientations of the luminescent molecules are uncorrelated. Here we present a theory in which their orientations are correlated such that nearby molecules tend to align, while their positions remain distributed homogeneously and without correlations. These correlations are assumed to be imposed by (local) order in the host medium.

In a typical experimental configuration,[10] also considered throughout this work, molecules are excited by a laser beam incident along the y axis of the lab frame and polarized parallel to the z axis. One obtains information on the transfer process from the fluorescence emission anisotropy

$$A = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp}), \tag{1.1}$$

observed in the x direction with intensities of components parallel ($I_{\parallel}$) and perpendicular ($I_{\perp}$) to the initial polarization. In the absence of any correlations, and for isotropic transfer rates, the time dependence of the anisotropy, after flash excitation at $t = 0$, is given by

$$A(t)/A(0) = \langle p_1(t) \rangle. \tag{1.2}$$

Here $\langle p_1(t) \rangle$ is the configurational average[12–17] of the probability that an initially excited molecule will also be excited at time t. The steady state analog of Eq. (1.2) has served as a basis for many previous studies.[6–9]

In this work, an expression for $A(t)$ is found for luminescent molecules that are embedded in a homogeneous two- or three-dimensional medium, which is in an axially symmetric phase with the xy plane as a symmetry plane, and which consists of axially symmetric molecules (e.g., a model membrane). Here, by two-dimensionality we mean that the centers of mass of the luminescent molecules are confined to a plane, whereas the molecules themselves need not be oriented within this plane. This may for instance describe a situation in which the molecules are embedded in many, relatively thin, parallel layers that are so far apart, that energy transfer only occurs within them. Instead of an isotropic probability density for the orientations of individual molecules, and thus of their emission dipoles, as is always considered, we assume that the only restrictions on the orientational singlet distribution, $f(\Omega)$, are imposed by the symmetries mentioned above. This guarantees a general axisymmetric distribution[18]:

$$f(\Omega) = \sum_{L \text{ even}} f_L P_L(\cos\beta); \qquad f_L = \frac{2L+1}{8\pi^2}\overline{P}_L, \quad \Omega = (\alpha, \beta, \gamma), \tag{1.3}$$

where P_L are Legendre polynomials and $\overline{P}_L$ are the order parameters of the phase. The usual Euler angles α, β, and γ fix the orientation of the molecule in the laboratory, by describing the rotation from the lab frame to the molecular frame, the z axis of the latter being identified with the molecular axis (see Fig. 1). The important new element in our theory is that we admit correlations between the orientations of the luminescent molecules, which will also be heavily restricted by the symmetries of the system. Finally we assume an isotropic multipole–multipole transfer rate

$$w_{ij} = w(r_{ij}) = (1/\tau)(R/r_{ij})^m \tag{1.4}$$

between molecules i and j at distance $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. R is the critical transfer distance, and τ the total lifetime of the excited state.

This paper is organized as follows. Section II contains a

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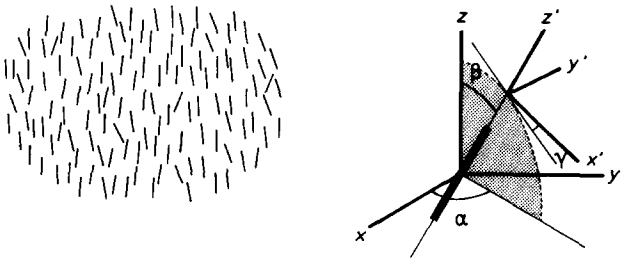

FIG. 1. Cross section of a typical system studied here, with nonisotropic orientational distribution (left). Characterization of the orientation Ω of an arbitrary molecule by the Euler angles α, β, and γ, which define the rotation from the lab frame (x,y,z) to the molecular frame (x',y',z') (right).

formulation of the problem, with a derivation of the general form, in which orientational correlations enter the theoretical analysis of the anisotropy (1.1). In Sec. III, theoretical expressions are obtained for the anisotropy in a system both with and without orientational correlations between molecules, and with the symmetries mentioned above. In Sec. IV, the anisotropy is analyzed for specific models of energy transfer. For a special choice of orientational correlations in these models, explicit numerical calculations are performed in Sec. V, which clearly demonstrate the effect of their inclusion upon the anisotropy. Complementary results have already been briefly reported elsewhere.[19] Section V also contains some concluding remarks. Some extensions of results obtained in Sec. II are given in the Appendix.

II. FORMULATION OF THE PROBLEM

In order to describe the transfer process, we will make the common assumption, that the initial excitation degree in the system is very low. As a result, one usually considers many large, isolated clusters of luminescent molecules, each existing of one initially excited molecule surrounded by different configurations of neighboring molecules. The process of energy transfer in one cluster is described by the coupled rate equations (CRE's) for the probability $p_i(t)$ of finding molecule i ($i = 1,2,...,N$) in the cluster to be excited at time t:

$$\frac{dp_i(t)}{dt} = -\sum_{j\neq i} w_{ij}\, p_i(t) + \sum_{j\neq i} w_{ij}\, p_j(t), \tag{2.1}$$

subject to the initial condition $p_i(0) = \delta_{i1}$. In practice, any observed fluorescence quantity will then be an average, denoted by $\langle(\cdots)\rangle$, over all possible configurations of the molecules in such a cluster, and one may write the anisotropy of fluorescence emission in terms of the probabilities $p_i(t)$ as

$$A(t) = \left\langle \sum_i p_i(t) g_1(\Omega_i) \right\rangle \Big/ \left\langle \sum_i p_i(t) g_2(\Omega_i) \right\rangle, \tag{2.2}$$

where

$$g_1(\Omega_i) = \cos^2\beta_i - \sin^2\beta_i \sin^2\alpha_i;$$
$$g_2(\Omega_i) = \cos^2\beta_i + 2\sin^2\beta_i \sin^2\alpha_i. \tag{2.3}$$

The orientation factors (2.3) follow from standard results for the emission probability of an excited molecule and from the fact, that the transition dipole must be parallel to the molecular axis in view of the axial symmetry.

If $\tilde{P}^{(k)}(X_1;X_2,...,X_k)$ denotes the k-particle distribution (normalized to unity) for the positions and orientations ($X_i \equiv \{\mathbf{r}_i, \Omega_i\}$) of the molecules 1,2,...,k ($1<k<N$) in configurations with one excited molecule ($i = 1$) at $t = 0$, then

$$\langle(\cdots)\rangle = \int dX_1 dX_2 \cdots dX_N \tilde{P}^{(N)}(X_1;X_2,...,X_N)\ (\ldots). \tag{2.4}$$

Let the usual k-particle distribution in the medium, without the condition that molecule 1 is excited at $t = 0$, be denoted $P^{(k)}(X_1,X_2,...,X_k)$ (also normalized to unity). Then

$$\tilde{P}^{(N)}(X_1;X_2,...,X_N) = \tilde{P}^{(1)}(X_1) P^{(N)}(X_1,...,X_N)/P^{(1)}(X_1). \tag{2.5}$$

This relation holds because $P^{(N)}(X_1,...,X_N)/P^{(1)}(X_1)$ equals the conditional distribution for the molecules 2,3,...,N, given that molecule 1 is at X_1. Multiplication by $\tilde{P}^{(1)}(X_1)$, the one-particle distribution for the initially excited molecules, then clearly gives the distribution for configurations with one excitation at $i = 1$ for $t = 0$. This then determines $\tilde{P}^{(N)}$ in terms of $P^{(N)}$ and the one-particle distributions $P^{(1)}$ and $\tilde{P}^{(1)}$, which are not identical because of the influence of the orientation on the absorption probability ($\propto \cos^2\beta_1$). For the spatially uniform system with the symmetries mentioned in Sec. I, it follows that

$$P^{(1)}(X_1) = (1/V) f(\Omega_1), \tag{2.6}$$

where f is given by Eq. (1.3), and, for uniform excitation of the sample,

$$\tilde{P}^{(1)}(X_1) = \frac{1}{V} \sum_{L\ \text{even}} \frac{3 f_L}{2\bar{P}_2 + 1} P_L(\cos\beta_1)\cos^2\beta_1$$
$$\equiv (1/V)\tilde{f}(\Omega_1), \tag{2.7}$$

where V is the volume of the sample (or the area in the two-dimensional case). Furthermore, since we assume that the positions of the molecules are distributed in an uncorrelated manner,

$$\int P^{(k)}(X_1,...,X_k) d\Omega_k = \frac{1}{V} P^{(k-1)}(X_1,...,X_{k-1}), \tag{2.8}$$

for $1<k<N$. As a result, the configurational average in Eq. (2.2) is not nearly as complex as Eq. (2.4) suggests. Using Eq. (2.8) repeatedly, together with Eqs. (2.5)–(2.7), one may derive that

$$\int \tilde{P}^{(N)}(X_1;X_2,...,X_N) d\Omega_3 ... d\Omega_N = \frac{1}{V^{N-2}} \frac{\tilde{f}(\Omega_1)}{f(\Omega_1)} P^{(2)}(X_1,X_2) \tag{2.9}$$

and

$$\int \tilde{P}^{(N)}(X_1;X_2,...,X_N) d\Omega_2 ... d\Omega_N = \frac{1}{V^N} \tilde{f}(\Omega_1). \tag{2.10}$$

In Sec. III it will turn out, that either of these reductions always occurs, and therefore, our description only involves the one-particle distributions (2.6) and (2.7), and the two-particle distribution

$$P^{(2)}(X_1,X_2) \equiv \frac{1}{V^2} G^{(2)}(X_1,X_2) = \frac{1}{V^2} G(\mathbf{r}_{12},\Omega_1,\Omega_2), \tag{2.11}$$

where $G^{(2)}$ depends on $\mathbf{r}_1$ and $\mathbf{r}_2$ only through $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ because the system is homogeneous. The absence of spatial correlations further leads to the condition [Eq. (2.8)]

$$\int G(\mathbf{r}_{12},\Omega_1,\Omega_2)d\Omega_2 = f(\Omega_1). \tag{2.12}$$

We will now derive the most general form for the pair correlation $G(\mathbf{r}_{12},\Omega_1,\Omega_2)$ that is appropriate for our system. For simplicity, and to be able to treat the two- and three-dimensional case simultaneously, we will assume that G is independent of the direction of $\mathbf{r}_{12}$. Then, the most general unrestricted form for G can be written as

$$G(r_{12},\Omega_1,\Omega_2) = \sum G^{m_1m_2;n_1n_2}_{L_1L_2}(r_{12})D^{L_1}_{m_1n_1}(\Omega_1)D^{L_2}_{m_2n_2}(\Omega_2), \tag{2.13}$$

where the summation runs over all indices that occur twice, and $D^L_{mn}(\Omega)$ represent the Wigner rotation matrices.[20] Expression (2.13) can be reduced considerably to obtain the most general form for G that is consistent with (i) intrinsic properties of G, (ii) the symmetry properties of the molecules and the phase, and (iii) the condition (2.12). The intrinsic properties are (a) symmetry with respect to permutation of the molecules 1 and 2; (b) reduction to the one-particle distribution after integration over X_2,

$$\int G(\mathbf{r}_{12},\Omega_1,\Omega_2)d\Omega_2 d\mathbf{r}_{12} = Vf(\Omega_1),$$

note that Eq. (2.12) is a stronger requirement; (c) normalization

$$\int G(\mathbf{r}_{12},\Omega_1,\Omega_2)d\Omega_1 d\Omega_2 d\mathbf{r}_{12} = V;$$

and (d) behavior at infinity

$$G(\mathbf{r}_2,\Omega_1,\Omega_2) \to f(\Omega_1)f(\Omega_2) \text{ for } r_{12} \to \infty.$$

The symmetry properties contained in (ii) have already been mentioned in Sec. I. Reduction of Eq. (2.13) resulting from the various symmetries can be achieved by a projection method,[21] outlined and applied previously in a very similar situation.[18] We will therefore not present the explicit calculations. Moreover, since the integration properties and the asymptotic behavior of G can be worked out in a straightforward manner, we just state the final form of G:

$$G(r_{12},\Omega_1,\Omega_2) = \sum G^{m_1}_{L_1L_2}(r_{12})D^{L_1}_{m_1,0}(\Omega_1)D^{L_2}_{-m_1,0}(\Omega_2), \tag{2.14}$$

with

$$G^{m_1}_{L_1L_2}(r) = 0 \text{ unless } L_1 + L_2 = \text{even}, \tag{2.15a}$$

$$G^{m_1}_{L_1L_2}(r) = G^{-m_1}_{L_2L_1}(r), \tag{2.15b}$$

$$G^0_{L0}(r) \text{ is independent of } r \text{ [from Eq. (2.12)]}, \tag{2.15c}$$

$$G^0_{L0} = \frac{1}{8\pi^2}f_L = \frac{2L+1}{(8\pi^2)^2}\overline{P}_L \quad \left(G^0_{00} = \frac{1}{(8\pi^2)^2}\right), \tag{2.15d}$$

$$\left.\begin{aligned} G^0_{L_1L_2}(r) &\to (8\pi^2)^2 G^0_{L,0}G^0_{L_20} \\ G^{m_1}_{L_1L_2}(r) &\to 0 \quad (m_1 \neq 0) \end{aligned}\right\} \text{ as } r \to \infty. \tag{2.15e}$$

By comparing Eqs. (2.13) and (2.14), one observes that all unnecessary indices have been omitted in the notation of the expansion coefficients in Eq. (2.14). Finally, it should be noted, that, for our theory, it is not necessary to take G independent of the direction of $\mathbf{r}_{12}$. The extensions of Eqs. (2.13)–(2.15) to the more general case in two and three dimensions are given in the Appendix.

III. ANALYTICAL EVALUATION OF THE ANISOTROPY

We now evaluate the anisotropy of fluorescence emission (1.1) for the experimental configuration described in Sec. I. If the population of excited molecules has an axisymmetric orientational singlet distribution, one can easily show[22] that A is additive in the sense that

$$A = \sum_n f_n A_n, \tag{3.1}$$

where n enumerates disjoint axisymmetric subsets of excited molecules and f_n is the fraction that the nth subset contributes to the total intensity, and A_n is the anisotropy of the emission of the nth subset alone. This additivity is based on the fact, that $I_\parallel + 2I_\perp = CI_{\text{total}}$ for a set of molecules with any axisymmetric singlet distribution, where C is a constant independent of further details of the distribution. The property (3.1) is especially useful for uncorrelated molecules.

A. Uncorrelated case

For completely uncorrelated luminescent molecules the two-particle distribution (2.11) is given by

$$G(\mathbf{r}_{12},\Omega_1,\Omega_2) = f(\Omega_1)f(\Omega_2), \tag{3.2}$$

where $f(\Omega)$ is the axially symmetric singlet distribution (1.3). The set of initially excited molecules has an axisymmetric singlet distribution [$\tilde{f}$ of Eq. (2.7)] at $t = 0$, and since we consider an isotropic transfer rate [Eq. (1.4)], the distribution of initially excited molecules that are still excited at time t has the same symmetry and even exactly the same form $\tilde{f}$ for all times. For the same reason, the excited molecules that were *not* excited at $t = 0$ have the axially symmetric distribution f for all times. Therefore, the additivity (3.1) is easily applied by distinguishing two subsets of excited molecules at time t: those that were excited initially (1), and those that were not (2). Thus

$$A(t) = f_1(t)A_1(t) + [1 - f_1(t)]A_2(t), \tag{3.3}$$

where, in fact, both $A_1(t)$ and $A_2(t)$ do not depend on time in view of the time independence of the orientational distributions. As is easily seen [cf. Eq. (2.2)], these subset anisotropies equal the quotient of the orientation factors g_1 and g_2, after averaging them over the distribution $\tilde{f}$ (for A_1) and f (for A_2), respectively. One then obtains

$$A_1 = \frac{36\overline{P}_4 + 55\overline{P}_2 + 14}{35(2\overline{P}_2 + 1)} \tag{3.4}$$

and

$$A_2 = \overline{P}_2. \tag{3.5}$$

These expressions generalize the well-known results $A_1 = 0.4$ and $A_2 = 0$ for an isotropic distribution to an arbitrary axially symmetric distribution. Finally, $f_1(t)$ is determined by the solution to the CRE's (2.1). It is easy to see that $f_1(t) = \langle p_1(t)\rangle$, the configurational average of the probability that an initially excited molecule is also excited at time t. We therefore arrive at

$$A(t) = (A_1 - \overline{P}_2)\langle p_1(t)\rangle + \overline{P}_2, \tag{3.6}$$

which indeed reduces to the result (1.2) for an isotropic distribution.

We may also consider the surrounding molecules (2,...,N) as traps [$w_{j1}=0$, and $w_{ij}=0 (i,j\neq 1)$], with fluorescence at another frequency than the donors (initially excited molecules $i=1$). In that case, one can measure both the anisotropy and intensity of trap fluorescence. For uncorrelated molecules these quantities are evidently given by

$$A_{\text{trap}} = \bar{P}_2 \tag{3.7}$$

and

$$I_{\text{trap}} = \langle 1 - p_1(t)\rangle e^{-t/\tau}, \tag{3.8}$$

where the solution p_1 of the CRE's is now different from that occuring in Eq. (3.6), since many transfer rates are zero.

B. Anisotropy in the presence of orientational correlations

In this case, the property (3.1) still applies, but is less useful, because the anisotropy of the second subset (molecules that were not excited at $t=0$) will depend on time in a nontrivial way, since the transfer rate depends on distance, and the distance to the initially excited molecule determines the orientational distribution of the surrounding molecules. Therefore, we prefer to evaluate A directly from Eq. (2.2). We will, again, derive results for two cases: in the first all molecules can transfer energy (pure donor system), in the second the initially excited molecules are surrounded by a huge majority of perfect traps, to which direct energy transfer occurs.

Since the molecules 2,3,...,N are identical we have in Eq. (2.2),

$$\left\langle \sum_i p_i(t) g_\nu(\Omega_i)\right\rangle = \langle p_1(t) g_\nu(\Omega_1)\rangle + (N-1)\langle p_2(t) g_\nu(\Omega_2)\rangle \tag{3.9}$$

($\nu=1,2$). The first term to the right should be omitted in the case of trap fluorescence. Since p_1 and p_2 only depend on positions (isotropic transfer rates), one can use Eqs. (2.9) and (2.10) in order to obtain a substantial simplification of the averages, as we anticipated in the previous section. We have

$$\langle p_1(t) g_\nu(\Omega_1)\rangle = \int \tilde{P}^{(N)}(X_1;X_2,\ldots,X_N) p_1(t) g_\nu(\Omega_1) dX_1 \ldots dX_N$$

$$= \frac{1}{V^{N-1}} \int p_1(t)\, d\mathbf{r}_{12}\ldots d\mathbf{r}_{1N} \int \tilde{f}(\Omega_1) g_\nu(\Omega_1) d\Omega_1.$$

The angular integrals have already been performed in Sec. III A, namely

$$\int \tilde{f}(\Omega_1) g_1(\Omega_1) d\Omega_1 = A_1$$

[see Eq. (3.4)] and

$$\int \tilde{f}(\Omega_1) g_2(\Omega_1) d\Omega_1 = 1.$$

Thus, introducing the positional average

$$\langle(\cdots)\rangle_{\text{pos}} \equiv \frac{1}{V^{N-1}} \int (\cdots) d\mathbf{r}_{12}\cdots d\mathbf{r}_{1N}, \tag{3.10}$$

one obtains

$$\langle p_1(t) g_1(\Omega_1)\rangle = A_1 \langle p_1(t)\rangle_{\text{pos}}, \tag{3.11a}$$

$$\langle p_1(t) g_2(\Omega_2)\rangle = \langle p_1(t)\rangle_{\text{pos}}. \tag{3.11b}$$

Note, that $\langle p_1(t)\rangle_{\text{pos}} = \langle p_1(t)\rangle$ since $p_1(t)$ does not depend on orientations. Similarly, using Eq. (2.9), one can evaluate

$$\langle p_2(t) g_\nu(\Omega_2)\rangle = \int \tilde{P}^{(N)}(X_1;X_2,\ldots,X_N) p_2(t) g_\nu(\Omega_2) dX_1\ldots dX_N$$

$$= \frac{1}{V^{N-1}} \int G(\mathbf{r}_{12},\Omega_1,\Omega_2) \frac{\tilde{f}(\Omega_1)}{f(\Omega_1)} \times p_2(t) g_\nu(\Omega_2) d\mathbf{r}_{12}\cdots dr_{1N}\, d\Omega_1\, d\Omega_2. \tag{3.12}$$

One may now substitute the form (2.14) for G, and g_1 and g_2 in terms of Wigner rotation matrices. Using the orthogonality relations of the latter, and the relations (2.15), one obtains

$$\langle p_2(t) g_1(\Omega_2)\rangle = \frac{\bar{P}_2}{1+2\bar{P}_2} \langle p_2(t)\rangle_{\text{pos}} + \frac{2}{25} \frac{(8\pi^2)^2}{1+2\bar{P}_2} \langle G^0_{22}(r_{12}) p_2(t)\rangle_{\text{pos}} \tag{3.13a}$$

and

$$\langle p_2(t) g_2(\Omega_2)\rangle = \langle p_2(t)\rangle_{\text{pos}}. \tag{3.13b}$$

It is natural (and also convenient for future comparison) to define

$$g^0_{22}(r) \equiv G^0_{22}(r) - \left(\frac{5}{8\pi^2}\right)^2 \bar{P}^2_2, \tag{3.14}$$

which approaches zero as $r\to\infty$ [see Eqs. (2.15d) and (2.15e)], and thus represents the part of G^0_{22} due to correlations. One then arrives at

$$A_d(t) = (A_1 - \bar{P}_2)\langle p_1(t)\rangle_{\text{pos}} + \bar{P}_2 + \frac{2}{1+2\bar{P}_2} \left(\frac{8\pi^2}{5}\right)^2 (N-1)\langle g^0_{22}(r_{12}) p_2(t)\rangle_{\text{pos}} \tag{3.15}$$

for the anisotropy of the pure donor system, and

$$A_t(t) = \bar{P}_2 + \frac{2}{1+2\bar{P}_2} \left(\frac{8\pi^2}{5}\right)^2 \langle g^0_{22}(r_{12}) p_2(t)\rangle_{\text{pos}} / \langle p_2(t)\rangle_{\text{pos}} \tag{3.16}$$

for the anisotropy of trap fluorescence. The denominator of Eq. (2.2) does not show up in Eq. (3.15), because

$$1 = \left\langle \sum_{i=1}^{N} p_i(t)\right\rangle_{\text{pos}} = \langle p_1(t)\rangle_{\text{pos}} + (N-1)\langle p_2(t)\rangle_{\text{pos}},$$

which is a direct consequence of the fact, that $I_\parallel + 2I_\perp \sim I_{\text{tot}}$ is constant for a pure donor system (apart from the overall decay with lifetime τ which has been factored out of the CRE's from the start). In the absence of orientational correlations

$$G^0_{22}(r) = (8\pi^2 G^0_{20}(r))^2 = \left(\frac{5}{8\pi^2}\bar{P}_2\right)^2,$$

or $g^0_{22}(r)\equiv 0$. Therefore, one sees immediately, that Eqs. (3.15) and (3.16) reduce to the expressions (3.6) and (3.7) for uncorrelated molecules. The intensity of trap fluorescence (3.8) is, of course, not affected by correlations, since it involves only p_1.

Note, that, as a result of the simple structure of g_1 and g_2 and the restrictions on G imposed by symmetries, the expressions for the anisotropy contain only one of the expansion coefficients of the general two-particle distribution function. It appears that this is even the case if one substitutes for G the more general form (A2) or (A5) into Eq. (3.12), and that the only changes, which then occur in the expressions following Eq. (3.12), are replacements of $G^0_{22}(r_{12})$ and $g^0_{22}(r_{12})$ by $G^{00}_{220}(r_{12})$ and

$$g^{00}_{220}(r_{12}) \equiv G^{00}_{220}(r_{12}) - \left(\frac{5}{8\pi^2}\overline{P}_2\right)^2,$$

respectively, in three dimensions, and by $G^{00}_{22}(r_{12})$ and

$$g^{00}_{22}(r_{12}) = G^{00}_{22}(r_{12}) - \left(\frac{5}{8\pi^2}\overline{P}_2\right)^2$$

in two dimensions. Note that all these expansion coefficients belong to the same expansion function $D^2_{00}(\Omega_1)D^2_{00}(\Omega_2)$, since $D^0_{00}(\Omega_{12}) \equiv 1$ and $\exp[-im\varphi_{12}] = 1$ for $m = 0$. In spite of the occurrence of only one coefficient in the expressions (3.14) and (3.15), quantitative evaluation of the terms due to correlations is not easy, as we will see in the next section.

IV. THE ANISOTROPY FOR SPECIFIC TRANSFER MODELS

So far we have not introduced specific solutions of the CRE's for $p_1(t)$ and $p_2(t)$ into our results (3.15) and (3.16) for the anisotropy of fluorescence emission. For uncorrelated molecules, only $p_1(t)$ and its positional average is needed. With orientational correlations present, the difficulty of obtaining quantitative results is greatly compounded by the fact, that one also needs a solution for $p_2(t)$. In addition, this solution should have a form that allows for configurational averages to be taken. Nevertheless, the anisotropy can be further analyzed in two simple models of energy transfer.

A. No back transfer model with correlations

In this model, back transfer to an initially excited molecule is completely neglected,[12] and molecules that surround an initially excited one have no opportunity to transfer energy to each other. Clearly, in a pure donor system, this model is a crude approximation, valid for small times and low density. It is, however, exact for donors surrounded by a huge majority of traps. Now the CRE's (2.1) reduce to

$$\frac{dp_1}{dt} = -\sum_{i=2}^{N} w_{1i}\, p_1(t), \tag{4.1a}$$

$$\frac{dp_i}{dt} = w_{1i}\, p_1(t) \quad \text{for} \quad i \geqslant 2, \tag{4.1b}$$

with the initial condition

$$p_i(0) = \delta_{i1}. \tag{4.1c}$$

Equation (4.1a) has as a solution

$$p_1(t) = \prod_{i=2}^{N} e^{-w_{1i}t}, \tag{4.2}$$

so that

$$\langle p_1(t)\rangle_{\text{pos}} = \int \prod_{i=2}^{N}\left(\frac{e^{-w_{1i}t}}{V}\right) d\mathbf{r}_{12}\cdots d\mathbf{r}_{1N} = \left\{\frac{1}{V}\int e^{-w_{12}t} d\mathbf{r}_{12}\right\}^{N-1}. \tag{4.3}$$

It is obvious that the factorization of the solution for p_1, in contributions from separate molecules (2,...,N), greatly facilitates the positional averaging procedure, as is demonstrated in Eq. (4.3). It is now easy to solve for p_2 by substitution of Eq. (4.2) into Eq. (4.1b). This solution, however, does not factorize, and the positional average is therefore difficult to perform. Since we do not need p_2 explicitly, but only $\langle g^0_{22}(r)p_2(t)\rangle_{\text{pos}}$, we evaluate this quantity directly. Because the molecular positions and orientations are taken constant in time (static limit),

$$\frac{d}{dt}\langle g^0_{22}(r_{12})p_2(t)\rangle_{\text{pos}} = \left\langle \frac{d}{dt}[g^0_{22}(r_{12})p_2(t)]\right\rangle_{\text{pos}} = \langle g^0_{22}(r_{12})w_{12}p_1(t)\rangle_{\text{pos}}. \tag{4.4}$$

Substitution of Eq. (4.2) yields an average over a product, which, at the expense of an extra time integration, reduces to

$$\langle g^0_{22}(r_{12})p_2(t)\rangle_{\text{pos}} = \int_0^t \left\{\frac{1}{V}\int w_{12}g^0_{22}(r_{12})e^{-w_{12}t'}dr_{12} \times\left[\frac{1}{V}\int e^{-w_{13}t'}d\mathbf{r}_{13}\right]^{N-2}\right\}dt'. \tag{4.5}$$

The anisotropies (3.15) and (3.16) then read

$$A_d(t) = \overline{P}_2 + (A_1 - \overline{P}_2)[K_1(t)]^{N-1} + \left(\frac{8\pi^2}{5}\right)^2 \frac{2}{1+2\overline{P}_2}(N-1)\int_0^t K_2(t')[K_1(t')]^{N-2}dt' \tag{4.6}$$

for the pure donor system, and

$$A_t(t) = \overline{P}_2 + \left(\frac{8\pi^2}{5}\right)^2 \frac{2}{1+2\overline{P}_2}(N-1) \times \int_0^t K_2(t')[K_1(t')]^{N-2}dt'/(1-[K_1(t)]^{N-1}) \tag{4.7}$$

for donors surrounded by traps. And the intensity of trap fluorescence is given by

$$I_t(t) = \{1 - [K_1(t)]^{N-1}\}e^{-t/\tau}. \tag{4.8}$$

Here we have defined the following quantities:

$$K_1(t) = \frac{1}{V}\int e^{-w(r)t}d\mathbf{r}, \tag{4.9a}$$

$$K_2(t) = \frac{1}{V}\int w(r)g^0_{22}(r)e^{-w(r)t}d\mathbf{r}. \tag{4.9b}$$

Finally, through some technical algebra, the thermodynamic limit $N, V \to \infty$, with $N/V \equiv \rho$ the constant (donor or trap) density (a surface density in two dimensions), can be obtained. For the anisotropy in Eq. (4.6), one thus finds in the case of multipole–multipole rates (1.4),

$$A_d(t) = \overline{P}_2 + (A_1 - \overline{P}_2)M_1(t) + \left(\frac{8\pi^2}{5}\right)^2 \frac{2}{1+2\overline{P}_2} \times \int_0^t \frac{\Delta\hat{\rho}}{m}(t')^{\Delta/m-1}M_2(t')M_1(t')dt', \tag{4.10a}$$

where t and ρ have been replaced by dimensionless quantities

t/τ and $\hat{\rho} = V_\Delta R^\Delta \rho$, with V_Δ the volume of a Δ-dimensional unit sphere ($\Delta = 2,3$). The functions M_1 and M_2 are defined by

$$M_1(t) = \exp\left[-\frac{\Delta}{m} \hat{\rho} t^{\Delta/m} \int_0^{\alpha^{-m} t} x^{-1-\Delta/m}(1-e^{-x})dx \right], \tag{4.10b}$$

which is the continuum limit of a well-known result,[23] and

$$M_2(t) = \int_0^{\alpha^{-m} t} g_{22}^0\left(R\left(\frac{t}{x}\right)^{1/m}\right) e^{-x} x^{-\Delta/m}\, dx. \tag{4.10c}$$

In introducing the parameter $\alpha \equiv a/R$, we have inserted a cutoff in the integrals over relative positions, which prevents molecules from being within a distance a of each other, where a is characteristic of molecular dimensions. One may consider this cutoff to be present in all integrals over relative positions encountered so far. For clarity of notation, we have mentioned it nowhere, before it was actually needed in the derivation of the quantitative results (4.10). Analogous, and equally extensive formulas in which precisely the same integrals, M_1 and M_2, occur, can be derived for $A_t(t)$ and $I_t(t)$. Further quantitative results can only be obtained by numerical integration.

B. Pure donor system in the direct transfer model

A somewhat better model[14] for solution of the CRE's in the pure donor system is obtained by allowing the initially excited donor $i = 1$ to interact with every other donor *with* back transfer, while donors 2, 3,..., N do not interact with each other. The CRE's, with symmetric rates given by (1.4), then read

$$\frac{dp_1}{dt} = -\left(\sum_{i\neq 1} w_{1i}\right) p_1 + \sum_{i\neq 1} w_{1i}\, p_i, \tag{4.11a}$$

$$\frac{dp_i}{dt} = w_{1i}\, p_1 - w_{1i} p_i \quad (i \neq 1), \tag{4.11b}$$

$$p_i(0) = \delta_{i,1}. \tag{4.11c}$$

After Laplace transformation $\mathscr{L}$ ($\tilde{p}(s) \equiv \mathscr{L}[p(t)]$) it is found[14] that

$$\tilde{p}_1(s) = \int_0^\infty e^{-sx} \prod_{i=2}^{N} \exp\left[-\frac{xsw_{1i}}{s+w_{1i}} \right] dx \tag{4.12}$$

and

$$\tilde{p}_2(s) = \frac{w_{12}}{s+w_{12}} \tilde{p}_1(s). \tag{4.13}$$

Since $\mathscr{L}$ and $\langle\ \rangle_{\rm pos}$ commute, it is clear that Eq. (3.15) yields

$$\tilde{A}_d(s) = \frac{\overline{P}_2}{s} + (A_1 - \overline{P}_2)\langle \tilde{p}_1(s)\rangle_{\rm pos} + \frac{2}{1+2\overline{P}_2}\left(\frac{8\pi^2}{5}\right)^2 (N-1) \times \langle g_{22}^0(r_{12})\tilde{p}_2(s)\rangle_{\rm pos}\ . \tag{4.14}$$

The positional average can again be reduced by virtue of the fact, that $\tilde{p}_1(s)$ and $\tilde{p}_2(s)$ factorize into (an integral over) a product of contributions from individual molecules. Taking the thermodynamic limit, one arrives at

$$\langle \tilde{p}_1(s)\rangle_{\rm pos} = \int_0^\infty e^{-sx} \times \exp\left\{ -\Delta\rho V_\Delta \int_a^\infty [1 - H(x,r)] r^{\Delta-1}\, dr \right\} dx, \tag{4.15}$$

and

$$(N-1)\langle g_{22}^0(r)\tilde{p}_2(s)\rangle = \int_0^\infty e^{-sx} \Delta\rho V_\Delta \int_a^\infty \frac{r^{\Delta-1} w(r)}{s+w(r)} g_{22}^0(r) H(x,r)\, dr \times \exp\left\{ -\Delta\rho V_\Delta \int_a^\infty [1 - H(x,r)] r^{\Delta-1} dr \right\} dx, \tag{4.16}$$

where

$$H(x,r) \equiv \exp\{ -xsw(r)/[s + w(r)] \}.$$

As in Sec. IV A, it is possible to transform to dimensionless quantities and the resulting integrals may in principle be evaluated numerically. But, in order to obtain the time-dependent anisotropy, a numerical inverse Laplace transformation would then have to be carried out. This clearly illustrates the limitations to what can be achieved theoretically. In the present model, one is still able to save the factorization of the solution, and hence perform the positional average, at the expense of a Laplace transformation. The inverse Laplace transformation, however, becomes extremely difficult. On the other hand, Eq. (4.14), together with Eqs. (4.15) and (4.16), itself represents a physical quantity of interest, since $(1/\tau)A_d[s = (1/\tau)]$ is the steady state anisotropy.[10]

V. NUMERICAL RESULTS AND DISCUSSION

In order to gain quantitative insight in the effect of correlations upon the emission anisotropy, we perform numerical calculations for the following heuristic two-particle correlation function:

$$G(r_{12},\Omega_1,\Omega_2) = \{ \chi(r_{12})\delta(\Omega_2 - \Omega_1) f(\Omega_1) + [1 - \chi(r_{12})] f(\Omega_1) f(\Omega_2) \}. \tag{5.1}$$

Here $\chi(r)$ is a function that completely determines the r dependence of the correlations. The range of χ should be [0,1], so that G is positive definite. The δ function in Eq. (5.1) is defined such that it does not distinguish between different values of the third Euler angle γ,[24] since the molecules are axially symmetric. If one chooses $\chi(a) = 1$ and $\chi(\infty) = 0$, expression (5.1) mimics correlations that tend to align nearby molecules and vanish at infinity. The typical length scale on which $\chi(r)$ falls to zero is now equivalent to the correlation length. We will choose, as a characteristic example,

$$\chi(r) = e^{-(r-a)/L}. \tag{5.2}$$

Thus, in order to demonstrate the effect of correlations, we do not specify the expansion coefficient $g_{22}^0(r)$ in Eq. (3.15) or (3.16) directly. Instead we choose the two-particle correlation function (5.1), with Eq. (5.2), whose physical meaning is intuitively clear. Of course, Eq. (5.1) obeys all the requirements discussed in Sec. II, and has therefore an expansion of the form (2.14). The relevant expansion coefficient (3.14), which occurs in Eqs. (3.15) and (3.16), is found to be

$$g_{22}^0(r) = \frac{2}{(8\pi^2)^2}\left(1 + \frac{10}{7}\overline{P}_2 + \frac{18}{7}\overline{P}_4 - 5\overline{P}_2^2\right)\chi(r). \quad (5.3)$$

Upon substitution of Eq. (5.3), with Eq. (5.2), into Eqs. (3.15) and (3.16), one obtains equations for anisotropies in terms of $\chi(r)$, which can be worked out in the thermodynamic limit, as was done in Sec. IV, for the two transfer models. Numerical calculations are performed for the no back transfer model, and Figs. 2 and 3 show some of the results thus obtained in two dimensions for an isotropic singlet distribution ($\overline{P}_2 = \overline{P}_4 = 0$) and a Förster transfer rate ($m = 6$). The solid curves in Fig. 2 show the anisotropy of donor fluorescence, $A_d(t)/A_d(0) = A_d(t)/A_1$ (only initially excited donors contribute at $t = 0$), for $\hat{\rho} = 1.0$, $\alpha = 0.1$ and various values of the rescaled correlation length $\Lambda = L/R$. The case $\Lambda = 0$ represents absence of correlations and corresponds to relation (1.2). Clearly, the anisotropy is influenced considerably by correlations. That this may have an important effect on the value of the critical transfer distance R as predicted from anisotropy measurements, can be illustrated by the following example. Imagine that one observes a pure donor system with given molecular size a, and of known density ρ. Suppose that the unknown value of R is such that $\hat{\rho} = 1.0$ and $\alpha = 0.1$ and, furthermore, that correlations given by Eqs. (5.1) and (5.2) with $\Lambda = 1.0$ are present, but that one is *unaware* of them. One chooses to analyze the data in terms of a no back transfer model, which should be reasonable for sufficiently small times. For $t \lesssim \tau$ the data are found to lie close to the solid curve with $\Lambda = 1.0$, $\hat{\rho} = 1.0$, and $\alpha = 0.1$, by which they should be fitted in view of the correlations. Instead they will be fitted for $t \lesssim \tau$ by the dashed–dotted curve with $\Lambda = 0$, $\hat{\rho} = 0.30$, and $\alpha = 0.18$,[25] since one is unaware of correlations and therefore ignores them. In this way one has underestimated R by 45%. Similar discrepancies are found at other reduced densities for $\Lambda = 1.0$. Calculations have also been carried out in three dimensions, for which similar features are observed. In that case one finds that R can be underestimated by as much as 30%. We reported these results earlier.[19]

For the trap fluorescence, confusion of uncorrelated and correlated systems is impossible, since in the first case the anisotropy would be constant in time. In these systems it may be possible to obtain experimentally the critical transfer distance from the intensity and the correlation length from the anisotropy of trap fluorescence. The solid curves in Fig. 3 give the anisotropy for $\hat{\rho} = 1.0$, $\alpha = 0.1$ and various values of Λ. These data demonstrate a strong dependence on the correlation length and thus underline the suitability of the anisotropy as a ruler for this quantity. Similar results are again found in three dimensions.[19]

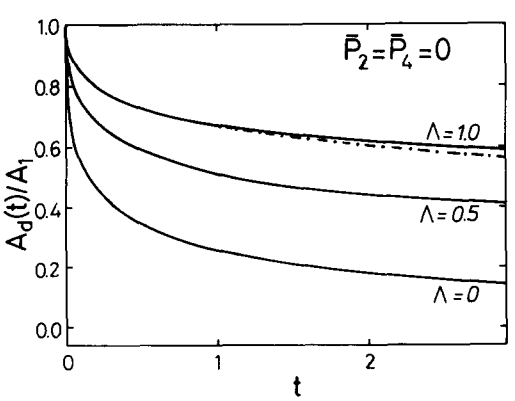

FIG. 2. $A_d(t)/A_1$ in two dimensions at some values of Λ for $\hat{\rho} = 1.0$, $\alpha = 0.10$, $m = 6$ (solid curves). A fit of the expression for the uncorrelated case ($\Lambda = 0$) to the solid curve with $\Lambda = 1.0$ yields $\hat{\rho} = 0.30$, $\alpha = 0.18$ (dashed–dotted curve). Part of the dashed–dotted curve cannot be distinguished from the solid curve. Time is given in units of the total lifetime.

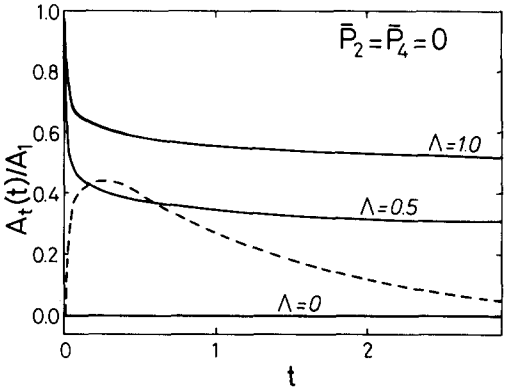

FIG. 3. $A_t(t)/A_1$ in two dimensions at some values of Λ for $\hat{\rho} = 1.0$, $\alpha = 0.10$, $m = 6$ (solid curve). Also shown is the trap intensity $I_t(t)$ in units of the total, i.e., donor and trap intensity (dashed curve). Time is given in units of the total lifetime.

A remark should be made concerning the behavior of $A_t(t)/A_1$ for small times. Since the intensity of trap fluorescence (dashed curve) equals zero for $t = 0$, it is hard to speak of the anisotropy at $t = 0$. One can, however, evaluate $\lim_{t \downarrow 0} A_t(t)/A_1$, and it turns out that (for $\overline{P}_2 = \overline{P}_4 = 0$) this limit equals

$$(m - \Delta)\alpha^{m-\Delta}\int_a^\infty r^{\Delta - m - 1}\exp[-(r-\alpha)/\Lambda]dr,$$

which in this case gives the values 0.94 and 0.97 for $\Lambda = 0.50$ and $\Lambda = 1.0$, respectively. The fact that these limits are so close to unity can be understood as follows. For very small times, only traps that are close to initially excited donors have a chance to be excited. These traps are within the correlation length so that they have a singlet distribution that closely resembles that of the initially excited donors.

Another remark is in order concerning the behavior of the anisotropies for large times. Clearly, in reality, the donor anisotropy will approach $\overline{P}_2$ for large times, because the excitations that have not decayed yet, by then have lost all memory of the initial orientation, as a result of many successive jumps through the system. Of course, our results (Fig. 2) do not predict this limit, because after the first jump the excitation remains on the same molecule so that a limit higher than $\overline{P}_2$ follows. This higher limit *is* correct for the trap fluorescence, for which it is also predicted, since our transfer model is exact for this system.

Finally it is clear that one would like to insert a better transfer model for the pure donor system into this theory, in order to investigate the influence of correlations. Obviously, correlations that tend to align nearby molecules always slow down the decay of the donor anisotropy and thus will, if they are ignored, cause an underestimated value for R. So, for other

transfer models, we expect qualitatively similar behavior. However, we do not know *a priori* whether the quantitative effects will be as drastic as discussed in this work. Although more sophisticated models exist,[12–17] it appears very difficult to derive $\langle \chi(r_{12})p_2(t)\rangle_{\rm pos}$ in the framework of any of these models.

APPENDIX

In this Appendix we give the extension of the most general form of the pair correlation $G(\mathbf{r}_{12},\Omega_1,\Omega_2)$ that includes a dependence on the direction of $\mathbf{r}_{12}$. In that case one must insert in the expansion of G an extra complete set of functions of this direction. In three dimensions such a set is provided by $D^L_{m0}(\Omega_{12})$, where $\Omega_{12}=(\varphi_{12},\theta_{12},0)$, θ_{12}, and φ_{12} being the usual polar angles in three dimensions. The unrestricted general form for G then reads [cf. Eq. 2.13)]

$$G(\mathbf{r}_{12},\Omega_1,\Omega_2) = \sum G^{m_1m_2m;n_1n_2}_{L_1L_2L} D^{L_1}_{m_1n_1}(\Omega_1) D^{L_2}_{m_2n_2}(\Omega_2) D^{L}_{m0}(\Omega_{12}). \quad \text{(A1)}$$

After working out all restrictions on G given by the properties (i)–(iii) in Sec. II, Eq. (A1) reduces to

$$G(\mathbf{r}_{12},\Omega_1,\Omega_2) = \sum G^{m_1m_2}_{L_1L_2L}(r_{12}) D^{L_1}_{m_1,0}(\Omega_1) D^{L_2}_{m_2,0}(\Omega_2) D^{L}_{-m_1-m_2,0}(\Omega_{12}) \quad \text{(A2)}$$

with

$$G^{m_1m_2}_{L_1L_2L}(r) = 0 \text{ unless } L_1+L_2+L = \text{even}, \quad \text{(A3a)}$$

$$G^{m_1m_2}_{L_1L_2L}(r) = (-1)^L G^{m_2m_1}_{L_2L_1L}(r), \quad \text{(A3b)}$$

$$\left.\begin{aligned} &G^{00}_{L_100}(r) \text{ is independent of } r \\ &G^{m_10}_{L_10L}(r) = 0 \text{ otherwise} \end{aligned}\right\}, \quad \text{(A3c)}$$

$$G^{00}_{L00} = \frac{1}{8\pi^2} f_L = \frac{2L+1}{(8\pi^2)^2}\bar{P}_L \quad \left(G^{00}_{000} = \frac{1}{(8\pi^2)^2}\right), \quad \text{(A3d)}$$

$$\left.\begin{aligned} &G^{00}_{L_1L_20}(r) \to (8\pi^2)^2 G^{00}_{L_100} G^{00}_{L_200} \\ &G^{m_1m_2}_{L_1L_2L}(r) \to 0 \text{ otherwise} \end{aligned}\right\} \text{ as } r\to\infty. \quad \text{(A3e)}$$

In two dimensions the direction of $\mathbf{r}_{12}$ is specified by only one angle φ_{12} and the unrestricted form for G is now

$$G(\mathbf{r}_{12},\Omega_1,\Omega_2) = \sum G^{m_1m_2m;n_1n_2}_{L_1L_2}(r_{12}) D^{L_1}_{m_1n_1}(\Omega_1) D^{L_2}_{m_2n_2}(\Omega_2) e^{-im\varphi_{12}}. \quad \text{(A4)}$$

The restrictions given in Sec. II now reduce this to

$$G(\mathbf{r}_{12},\Omega_1,\Omega_2) = \sum G^{m_1m_2}_{L_1L_2}(r_{12}) D^{L_1}_{m_10}(\Omega_1) D^{L_2}_{m_20}(\Omega_2) e^{i(m_1+m_2)\varphi_{12}} \quad \text{(A5)}$$

with

$$G^{m_1m_2}_{L_1L_2}(r) = 0, \text{ unless } L_1+L_2+m_1+m_2 = \text{even}, \quad \text{(A6a)}$$

$$G^{m_1m_2}_{L_1L_2}(r) = (-1)^{m_1+m_2} G^{m_2m_1}_{L_2L_1}(r_{12}), \quad \text{(A6b)}$$

$$\left.\begin{aligned} &G^{00}_{L_10}(r) \text{ is independent of } r \\ &G^{m_10}_{L_10}(r) = 0 \text{ otherwise} \end{aligned}\right\}, \quad \text{(A6c)}$$

$$G^{00}_{L0}(r) = \frac{1}{8\pi^2} f_L = \frac{2L+1}{(8\pi^2)^2}\bar{P}_L \quad \left(G^{00}_{00} = \frac{1}{(8\pi^2)^2}\right), \quad \text{(A6d)}$$

$$\left.\begin{aligned} &G^{00}_{L_1L_2}(r) \to (8\pi^2)^2 G^{00}_{L_10} G^{00}_{L_20} \\ &G^{m_1m_2}_{L_1L_2}(r) \to 0 \text{ otherwise} \end{aligned}\right\} \text{ as } r\to\infty. \quad \text{(A6e)}$$

As in Sec. II, all unnecessary indices have been omitted from the final expansions (A2) and (A5). Note that the results indeed reduce to Eq. (2.14) with Eq. (2.15) if one assumes that G in Eqs. (A2) and (A5) does not depend on Ω_{12} and φ_{12}, respectively.

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[24] This means that the expansion of the δ function in Wigner rotation matrices reads:

$$\delta(\Omega_2-\Omega_1) = \sum_{L,m} \frac{2L+1}{8\pi^2} (-)^m D^L_{m0}(\Omega_2) D^L_{-m0}(\Omega_1).$$

[25] Any $\Lambda = 0$ fit only depends on α for very small times $t \ll \alpha^m$ (cf. Ref. 23). The overall fit is therefore not very sensitive to the precise value of a.